PEROXIDE MEASUREMENTS FOR ACE ASIA
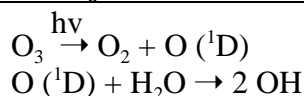**PROJECT DESCRIPTION**

Objectives

The Aerosol Characterization Experiment (ACE) planned for 2001-2004 in Asia, is designed to improve our understanding of the size and geographical distribution, chemical composition, seasonal variability, sources, sinks and radiative properties of anthropogenic aerosols. Sulfate is one of the principal constituents of aerosol particles in this region, and a substantial portion of the sulfate aerosol has its origin in oxidation of gaseous SO_2. We propose to determine ambient concentrations of gaseous hydroperoxides, which are believed to be important oxidants for SO_2 in atmospheric water droplets and aerosols. In addition to adding to the relatively sparse set of observations in the region, these measurements will be used to determine the relative importance of various oxidative pathways, and will provide necessary input for model calculations aimed at understanding aerosol formation mechanisms.
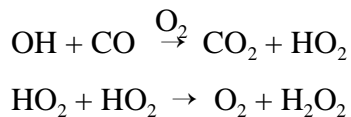
Introduction

Peroxides are ubiquitous in the troposphere as termination products of the odd hydrogen radical mechanism initiated by ozone photolysis. Hydroxyl radicals produced from ozone photolysis in the presence of water vapor react with CO and VOCs to form HO_2 and RO_2 radicals. In the absence of competing reactions, these radicals self react to form hydroperoxides. Laboratory experiments have shown the reaction of ozone with alkenes in moist air to be an additional source of H_2O_2 and hydroxyalkyl hydroperoxides via a nonradical pathway *(Becker et al., 1990; Hewitt and Kok, 1991; Gäb et al., 1995)*. These reactions are illustrated in Table 1.
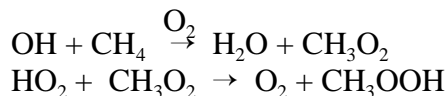
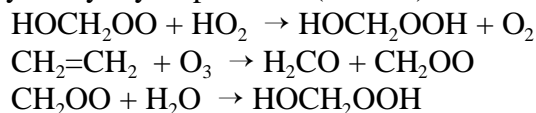> *Table 1   Sources of most abundant atmospheric peroxides*
>
> $$O_3 \xrightarrow{h\nu} O_2 + O\,(^1D)$$
> $$O\,(^1D) + H_2O \rightarrow 2\,OH$$
>
> hydrogen peroxide
>
> $$OH + CO \xrightarrow{O_2} CO_2 + HO_2$$
> $$HO_2 + HO_2 \rightarrow O_2 + H_2O_2$$
>
> methyl hydroperoxide (MHP)
>
> $$OH + CH_4 \xrightarrow{O_2} H_2O + CH_3O_2$$
> $$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH$$
>
> hydroxymethyl hydroperoxide (HMHP)
> $$HOCH_2OO + HO_2 \rightarrow HOCH_2OOH + O_2$$
> $$CH_2=CH_2 + O_3 \rightarrow H_2CO + CH_2OO$$
> $$CH_2OO + H_2O \rightarrow HOCH_2OOH$$

1

Two review articles have summarized peroxide measurement techniques and field observations through 1990. Since then, a number of ground- and aircraft-based peroxide measurements, some using high pressure liquid chromatography (HPLC) to quantitate individual peroxides, have demonstrated that organic hydroperoxides can constitute a significant fraction of the total *(Hewitt and Kok, 1991; Enders et al., 1992; Heikes et al, 1992; Lee at al., 1993; Weller and Shrems, 1993, Ayers et al., 1996, MacDonald et al, 1995; Fels and Junkermann 1994; Tremmel et al., 1994, Weinstein-Lloyd et al., 1998).* Although the formation of higher molecular weight hydroperoxides is expected to occur, H_2O_2, methyl hydroperoxide (MHP), and hydroxymethyl hydroperoxide (HMHP) are the major hydroperoxides so far identified in significant concentrations in the atmosphere. It should be noted that peroxide measurement techniques are still in the development phase. The HPLC technique provides reasonably unambiguous identification of individual peroxides, but full characterization of these species is not possible with the often-used dual channel catalase system.

The active photochemistry and abundant VOCs characteristic of urban environments produce high concentrations of the peroxy radical precursors to peroxides. However, these regions also have high concentrations of NO_x which compete for peroxy radicals, favoring the formation of NO_x oxidation products over peroxides (*Kleinman, 1991; Kleinman et al., 1997; Jacob et al., 1995*). Peroxide concentrations and ratios of peroxides to NO_x oxidation products have been used to indicate whether tropospheric ozone formation is limited by the availability of NO_x or hydrocarbons (*Sillman, 1995, Sillman et al., 1998*) .

High Henry's Law solubilities of H_2O_2 and HMHP, K_h on the order of 10^5 M/atm, respectively (*Zhou and Lee, 1992; Staffelbach and Kok, 1993; O'Sullivan et al., 1996)* result in efficient transfer of these species into water droplets, while MHP, $K_h \sim 10^3$ (*Lind and Kok, 1994; O'Sullivan, 1996*), is less soluble. Thus, wet scavenging and subsequent aqueous-phase reactions care are an important sink for atmospheric peroxides. Other sinks include dry deposition, photolysis and reaction with OH reaction. In the absence of deposition, peroxides can persist for several days in the troposphere.

Peroxides are largely responsible for the aqueous-phase oxidation of atmospheric SO_2 in the northeastern U.S., where precipitation is acidic (*Penkett et al., 1979; Martin and Damschen, 1981; Daum et al., 1984, Macdonald et al., 1995*). Other oxidants may contribute to SO_2 oxidation in atmospheric water droplets and aerosols, with reaction rates that are highly dependent on chemical composition of the medium, including pH and the availability of metal ion catalysts. In a theoretical cloud containing 1 µM Fe(III), e.g., oxidation by O_3 and by O_2 catalyzed by Fe(III), are comparable in efficiency to that by peroxide at pH 5 - 6; H_2O_2 oxidation dominates by orders of magnitude at lower pH *(Martin, 1994).* Rate coefficients for the reaction of SO_2 with the three most abundant peroxides are all the same order of magnitude *(Lind et al., 1987; Zhou and Lee, 1992).* However, the lower solubility of MHP and lower natural abundance of HMHP suggest that H_2O_2 will be the most important oxidant.

Gaseous SO_2 in the marine boundary layer (MBL) may have been produced by oxidation of DMS or by combustion processes. Gas-phase reaction with OH to form H_2SO_4 may be the source of new sulfate-containing aerosol particles. In contrast, aqueous-phase reactions in cloud droplets or in hygroscopic aerosols will form sulfate in pre-existing, larger particles. These competing processes influence the number of cloud condensation nuclei (CCN) that determine

the radiative properties of clouds *(Hering and Friedlander, 1982; Sievering, 1991)*.

Previous Peroxide Measurements

Since the early 1990's, we have conducted peroxide measurements during ground campaigns in Metter and Atlanta, Georgia (SOS 1992), on Long Island, NY (NARSTO 1997) and in air campaigns in Halifax, NS (NARE 1993), Nashville, TN, (SOS 1995), LI, NY (NARSTO '96) and Phoenix, AZ (1998). Our studies mostly have been concerned with understanding the mechanism of tropospheric ozone formation, and have been confined to geographical regions where O_3 is problematic. Principal observations from these studies are consistent with our understanding of peroxide sources and sinks, and are summarized below:

- At ground level, peroxide concentrations exhibit a diurnal variation consistent with higher midday photochemical production and rapid losses to wet surfaces at night *(Lee et al., 1993)*
- H_2O_2 concentrations decrease rapidly at the onset of precipitation events due to their high aqueous solubility. MHP, which is less soluble, does not decrease to the same extent *(Lee et al., 1993)*
- In the free troposphere (FT), where deposition and reaction of radical precursors with NO_x are unimportant, peroxide concentration is dominated by the concentration of its precursors, ozone and water vapor *(Weinstein-Lloyd et al., 1996)*
- While peroxides may be depleted in the nocturnal boundary layer (NBL), vertical soundings often reveal high peroxide concentrations in the residual BL that act as a reservoir, mixing peroxides down as daytime convection begins *(Weinstein-Lloyd et al., 1998)*
- Vertical profiles of H_2O_2 frequently exhibit maxima near the top of the boundary layer, which can be attributed to the combination of lower production in dryer air aloft, and surface deposition below. MHP profiles frequently follow those of H_2O_2, illustrating the free-radical source for both. When HMHP is measurable, concentrations generally are higher near the ground, consistent with a surface source, i.e., biogenic alkenes *(Weinstein-Lloyd et al., 1998)*.
- In photochemically aged air advected over the North Atlantic ocean in summer, peroxide can grow to high concentrations (>12 ppbv) in stable layers isolated from the ocean surface *(Weinstein-Lloyd et al., 1996)*
- In urban and power plant plumes, reaction of HO_2 radicals with NO_x competes effectively with HO_2 self-reaction, favoring production of NO_y at the expense of peroxides. Concentrations of peroxide in plume often are lower than background due to photochemical and chemical losses *(Weinstein-Lloyd et al., 1998)*.
- In Phoenix' dry atmosphere, low peroxide concentrations can be attributed in part to low OH concentration, a direct result of low water vapor concentration *(Nunnermacker et al., 2000; Kleinman et al., 2000)*.

A number of peroxide measurements in the remote marine boundary layer (MBL) are relevant to the ACE-Asia region. Heikes et al. *(1996)* determined H_2O_2 and MHP in an aircraft

mission over the western north Pacific during the PEM-West A mission in Fall 1991. He observed between 1 and 2 ppbv total peroxide near the Asian continent, with a significant (30 - 50%) contribution from MHP. Maximum peroxide concentrations were observed at altitudes between 2 and 3 km. Although median concentrations of both species were lower during PEM WEST-B in January and February 1993, unusually high values (>10 ppbv) were observed in recent continental outflow near Asia. *(O'Sullivan et al., 1993).* Thompson et al. *(1993)* measured total peroxide concentrations around 1 ppbv on a cruise in the equatorial Pacific MBL during SAGA-3 in July and August 1978, with equal contributions from H_2O_2 and MHP. Ayers et al. *(1996)* reported monthly mean peroxide concentrations between 0.2 and 1.4 ppbv at a ground site at Cape Grim, Tasmania with maximum values in November and December. Diurnal profiles were consistent with production through ozone photolysis during the day and losses to the ocean surface at night. Back trajectories suggested some prior contact with anthropogenic sources at this site. Instrument problems prevented the unambiguous determination of MHP, but the authors concluded that organic peroxides made a very significant contribution to the total and should not be ignored. Weller and Schrems *(1993)* determined gaseous peroxide aboard the vessel Polarstern during winter 1991/1992 in the remote Atlantic. They observed concentrations between 0.2 and 2.0 ppbv, with 20-35% contribution from ROOH, and a broad maximum between the Tropics of Cancer and Capricorn. These authors reported a 30% peroxide loss at the instrument inlet, despite efforts to protect the inlet from sea spray. Similar concentrations and latitudinal trends were observed in the same region in the Fall of 1990 *Slemr and Tremmel (1994)*, with a 48% average contribution of ROOH to total peroxide. Unusually high concentrations, associated with downward atmospheric motion, were ascribed to peroxide formation near cloud tops, with associated enhanced photochemical activity. In Trace A, during the Fall of 1992, Heikes et al. *(1996)* observed median peroxide concentrations around 2 ppbv in the MBL and 4.4 ppbv in the FT. Here too, MHP was a significant proportion of the total (50% in the MBL and 23% in the FT).

These measurements demonstrate that hydroperoxides will be present at ppbv concentrations in the ACE Asia region, and should contribute significantly to oxidative processes. Moreover, organic peroxides are likely to constitute a significant and variable proportion of the total. To understand sulfate production, the abundances of individual peroxides, together with their unique solubilities and reactivities, ought to be incorporated into model calculations. It would be most desirable to have both ground-based and aircraft sampling of these species.

Previous Relevant Aerosol Studies

During ACE I, *Sievering et al. (1999*) demonstrated that ozone was a principal oxidant for SO_2 in sea salt aerosol water (SSAW) initially at pH 8. As oxidation proceeded and pH dropped, peroxides and other species were expected to contribute to the oxidation. These investigators concluded that 35% of nss sulfate in sea salt aerosol water arises from ozone oxidation, a value comparable to that produced by homogeneous cloud conversion. Gurciullo et al. *(1999)* modeled the relative contribution of SSAW and cloud processing to nss sulfate concentrations in particles of 0.4 to 16 µm diameter at this site. Using assumed background concentrations of 0.5 ppbv H_2O_2 and 30 ppbv O_3, they found that peroxide contributed only 4%

to nss production.

The conversion of gaseous species to sulfate in cloud was the subject of an extensive field study in England in 1993 *(Choularton et al., 1997)*. The Great Dun Fell site, which has a summit cap cloud approximately 60% of the year, was used to study the modification of aerosol composition and size by passage through the cloud. *(Laj et al. 1997a)* The investigators found a significant increase in sulfate in the aerosol population downstream of the cloud compared to upstream, with oxidation of SO_2 occurring mostly through reaction with H_2O_2. Consumption of either H_2O_2 or SO_2 could limit sulfate production, depending upon efficiency of entrainment of air into the cloud. There was evidence for in-cloud production of H_2O_2 through photolysis as well *(Laj et al.,, 1997b)*.

Cheju Island is a valuable site for observing atmospheric chemistry during the ACE program. In spring, flows from northern and central China, with the associated dust storms and anthropogenic impact lead to the high aerosol concentrations *(Chen et al., 1997)* Cheju has been the site of a number of earlier measurement programs. Trace gases (SO_2, O_3, NO and NO_x) and total suspended particles (TSP) were monitored in March and April of 1994 *(Kim et al., 1998)*. Analysis of the TSP showed sulfate to be the greatest constituent of the water soluble ions, with over 90% comprising nss. Most of the back trajectories during this period originated on the Asian continent. Arimoto *(1996)* observed relationships between nss sulfate, trace metals and nitrate that indicated a primarily anthropogenic source for the sulfate. In a seasonal study at Cheju, Carmichael *(1996)* found that spring dust storms were associated with precipitation of elevated pH. Dust at the source was primarily carbonate, but included sulfate and nitrate as major constituents farther away, having been produced by reaction of gas-phase species during transport.
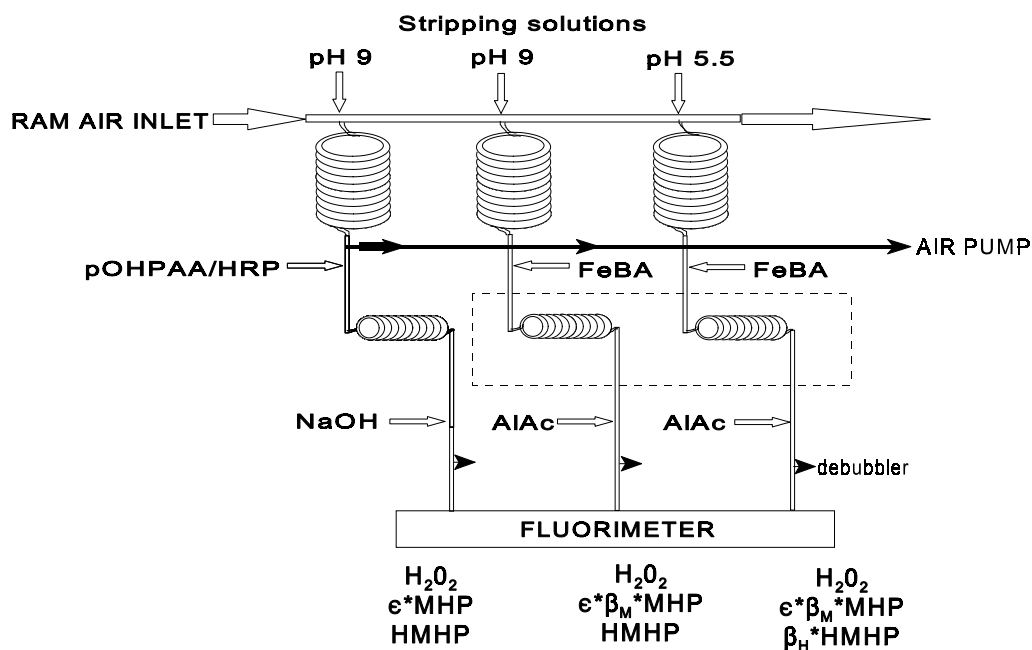
General Plan

A cloud cap study at Cheju Island, similar to those conducted at the Great Dun Fell site in England *(Choularton et al., 1997)* has been proposed as an ACE Asia activity. The study will include a characterization of the size distribution and chemical composition of aerosol advected from Asia. Peroxides will be measured, along with the concentrations of other trace gases at a site upstream of the cap cloud. The results will be used to interpret the role of cloud processing on aerosol properties and chemical composition, including sulfate formation.

Method

Peroxides will be determined using BNL's three channel peroxide analyzer. The instrument is a modification of the continuous flow analyzer designed by Kok and Lazrus *(Kok et al, 1986, Lazrus et al., 1986)*, employing glass coil scrubbers to transfer gaseous peroxide into the aqueous phase, with subsequent continuous flow derivitization to produce fluorescent products. Baselines are established by directing air through a hopcalite cartridge. Signal intensity in the field is calibrated with aqueous standards; these are verified in the laboratory with gas-phase standards. Using three channels, we can distinguish hydrogen peroxide (H_2O_2), methyl hydroperoxide (MHP) and hydroxymethyl hydroperoxide (HMHP) by exploiting their different reactivities and stabilities at high pH. A schematic diagram of the instrument appears below; reaction conditions are summarized in the Table 2.

3-CHANNEL PEROXIDE ANALYZER
BROOKHAVEN NATIONAL LAB

Stripping solutions

pH 9   pH 9   pH 5.5

RAM AIR INLET

pOHPAA/HRP →   ← FeBA   ← FeBA   → AIR PUMP

NaOH →   AlAc →   AlAc →   → debubbler

FLUORIMETER

H_2O_2
ϵ*MHP
HMHP

H_2O_2
ϵ*β_M*MHP
HMHP

H_2O_2
ϵ*β_M*MHP
β_H*HMHP

Table 2   Three-Channel Peroxide Analyzer

Channel	scrubbing solution	fluorescence reagent	enhancing reagent
1	pH 9	pOHPAA/HRP	NaOH
2	pH 6	FeBA	Al-acetate
3	pH 9	FeBA	Al-acetate

Channel 1 uses the well-known peroxidase enzyme-catalyzed reaction with p-hydroxyphenylacetic acid (pOHPAA/HRP) to produce a fluorescent dimer, and fluorescence is enhanced by raising the pH subsequent to dimer formation. This channel gives a signal proportional to total peroxide. In a 2nd channel, a Fenton reagent consisting of a mixture of Fe(II) and benzoic acid (BA) converts H_2O_2 into fluorescent hydroxybenzoic acids via a two step reaction involving hydroxy radical:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH$$
$$OH + BA \rightarrow OHBA$$
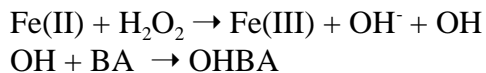
Fluorescence intensity in this channel is enhanced by the addition of Al(III) in acetate buffer. In channel 2, organic peroxides (ROOH) would produce OR radicals, but the RO-benzoic acid products do not fluoresce, so channel 2 gives a measure of H_2O_2 alone. The difference between Channels 1 and 2 give a measure of ROOH. In a third channel, we also use FeBA chemistry, but scrubbing solution is maintained at a high pH to rapidly hydrolyze HMHP to H_2O_2 prior to reaction. Thus the difference between channels 2 and 3 yields HMHP and MHP mixing ratios. Further details about the instrumentation can be found in the references *(Lee et al, 1990; Lee at al, 1994)*.

Along with other investigators, we have observed substantial decomposition of peroxide in inlet lines during ground-based measurements (*Lee et al., 1991; Watkins et al., 1995a; 1995b*). Losses are especially noticeable under conditions of high humidity and high aerosol loading, such as are expected in the ACE-Asia experiment. Our instruments have "inletless" samplers for ground based measurements - rather than bringing ambient air indoors to the instrument, we mount the coil scrubbers outdoors and draw air directly into the scrubbing solution for subsequent delivery to the instrument. This largely eliminates sampling losses.

Currently, the detection limit (DL) for each channel of the peroxide analyzer, based on 3σ baseline noise, is 25 pptv. Uncertainties associated with converting aqueous standards to gas-phase concentrations, including temperature variation and evaporative losses, typically amount to 15%. While 100% of the H_2O_2 and HMHP are sampled under our experimental conditions, MHP is only partially soluble, and the reported uncertainty in its Henry's Law constant is 20% *(Lind and Kok, 1994)*. These factors result in an operational DL close to 150 pptv for each species in the continuous mode. Although data is acquired at 0.1 Hz, liquid transfer and aqueous reactions limit response time to approximately one minute. We have two versions of the three-channel peroxide analyzer, one designed for aircraft and one for ground operation. We are developing an autosampler- based modification for collection that will have a longer sampling time (10 - 30 minutes), better DL, and will require less attention.

Significance

The measurement program suggested here will extend peroxide observations into a region where currently they are sparse. These measurements will identify regions where peroxides or other oxidants limit SO_2 oxidation. Models of sulfate production include peroxide concentrations as a parameter. The proposed peroxide measurements can be used to constrain model inputs, or alternatively to verify model-generated peroxide concentrations.

Relation to long term goals and present state of knowledge

We have a ten-year record of peroxide field measurements at sites in the eastern United States and Canada, and have used these measurements to gain a better understanding of atmospheric photochemistry as it relates to ozone production. We extended our understanding of these processes in a recent study in Phoenix, AZ, where the ambient mix of hydrocarbons, water vapor and NO_x differed greatly from those typically encountered in the eastern United States.

While ozone production is not the focus of the ACE-Asia study, sufficient trace gas measurements will be available to explore the relationships among ozone and its precursors in this new region.

A second goal relates to instrument development and performance. Although they have been conducted for fifteen years, field measurements of peroxides are by no means routine. As discussed above, organic peroxides are expected to constitute a significant portion of the total, and should be determined separately. This program will provide the opportunity for us to test instrument performance in a new environment in the MBL. Informal correspondence suggests that several additional groups will propose peroxide measurements using a number of different analytical methods during ACE Asia and the overlapping TRACE mission. This will provide a unique opportunity to conduct much-needed instrument intercomparisons.

Educational Impact

The State University of New York College at Old Westbury was founded in 1965. The youngest of SUNY's fourteen undergraduate colleges, Old Westbury has a tradition of attracting minorities, women and older students and those interested in non-traditional modes of learning. Of the present enrolment of approximately 3000 students, 43% are minorities (African American and Hispanic) and 53% are female. Science faculty have been conducting research with undergraduates for twenty years under a number of NSF, NIH and New York State Education - funded programs. The College has made a substantial impact on the number of underrepresented minorities earning degrees in the sciences, and much of this success can be attributed to our students' exposure to research. This proposal includes funds to support one undergraduate participant. The student will work on instrument performance in the lab prior to, and data analysis and interpretation after the trip, and hopefully will attend conferences where the results are discussed. If sufficient travel funds are available, participation in the actual field experiment would be an invaluable experience.